

Joshua S. Salafsky and Kenneth B. Eisenthal  
Serial No.: 09/731,366  
Filed: December 6, 2000  
Page 8

REMARKS

Claims 1-28 and 33-38 are pending in the subject application. By this Amendment, applicants have amended claims 21, 28 and 34. Accordingly, claims 1-28 and 33-38 are pending in the subject application.

Rejection Under 35 U.S.C. § 112, second paragraph

On page 2 of the October 23, 2003 Office Action, the Examiner rejected claims 21-28 and 33-38 under 35 U.S.C. § 112, second paragraph, as allegedly failing to particularly point out and distinctly claim the subject matter which applicants regard as their invention. Specifically, the Examiner alleged that in claim 21, part c) "a signal generated" is vague and indefinite and it is unclear what relationship exists between the second harmonic-active label and the signal generated using a surface selective technique; in claim 28, line 6 "can be" is vague and indefinite; and in claim 34, part (b) "a signal generated" is vague and indefinite.

In response, applicants have amended the claims to more clearly define their invention. As amended, applicants' claims satisfy the requirements of 35 U.S.C. § 112, second paragraph.

Rejections Under 35 U.S.C. §§ 102(b) and 103

In Section 4 of the October 23, 2003 Office Action, the Examiner maintained the rejection of claims 1-4, 7, 8, 12, 13, 21, 23, 27, 28, 33, 34, 36 and 37 as allegedly anticipated by Quinn et al. (European Patent Application No. 0 740 156), for the reasons set forth in the April 7, 2003 final Office Action.

In Sections 7-13 of the October 23, 2003 Office Action, the Examiner also maintained the multiple rejections under 35 U.S.C. § 103 all of which were over Quinn et al. along with

Joshua S. Salafsky and Kenneth B. Eisenthal  
Serial No.: 09/731,366  
Filed: December 6, 2000  
Page 9

various secondary references, for the reasons set forth in the April 7, 2003 final Office Action.

In Section 16 of the October 23, 2003 Office Action, the Examiner noted applicants' previous remarks about Quinn et al., but alleged that the remarks are not found persuasive. Specifically, the Examiner took the position that Quinn et al. reads on applicants' newly added limitation (i.e. an unlabeled molecule at the interface is undetectable using the surface selective technique) because one skilled in the art would recognize that the second harmonic label would require the second harmonic generation to be detected and if there is no such second harmonic generation label attached to the molecule, such a molecule would not be detected by second harmonic generation. Therefore, it is the Examiner's position that Quinn et al. reference still reads on the instantly recited claims.

During a December 2, 2003 telephone conference between Examiner Gary Counts, Supervisory Examiner Long Le, and the undersigned, Quinn et al. was discussed in more detail. Specifically, the undersigned pointed out to both Examiners that Quinn et al. use a reporter molecule to resonantly enhance a signal that is already present. Quinn et al. state that the "[s]econd-order optical processes originate from the field and structural discontinuity at the interface" [Quinn et al., column 2, lines 31-33], and a reporter molecule is used to resonantly enhance the surface nonlinear susceptibility [Quinn et al., column 2, lines 46 to 57]. As clarified in applicants' claims, applicant's invention uses a second harmonic-active label to produce a signal that is not present in the absence of the label, not merely to enhance an existing signal.

Therefore, Quinn et al. does not anticipate applicants'

Joshua S. Salafsky and Kenneth B. Eisenthal  
Serial No.: 09/731,366  
Filed: December 6, 2000  
Page 10

invention as recited in the amended claims. Furthermore, Quinn et al., alone or in combination with the disclosures of the secondary references, does not teach or suggest applicants' invention as recited in the amended claims because the deficiencies of Quinn et al. are not remedied by the secondary references.

During the December 2, 2003 telephone conference, both Examiner Gary Counts and Supervisory Examiner Long Le agreed that applicants' claims recite subject matter that is patentable over Quinn et al. However, the Examiners requested applicants to provide references which confirm that not all molecules are detectable using a given surface selective technique. In response, applicants attach hereto as **Exhibits A-D** excerpts from articles which clearly show that not all molecules are detectable using a given surface selective technique. Thus, applicants' recitation that an unlabeled molecule at the interface would be undetectable using a given surface selective technique clearly distinguishes applicants' claims from Quinn et al.

Accordingly, applicants respectfully request that the Examiner reconsider and withdraw the rejections under 35 U.S.C. §§ 102 and 103 over Quinn et al. set forth in the October 23, 2003 Office Action.

**Rejections Under 35 U.S.C. § 102(e)**

On page 4 of the October 23, 2003 Office Action, the Examiner rejected claims 1-4, 6, 12, 13, 21-23, 34 and 36-38 as allegedly anticipated by Schultz et al. (U.S. Patent No. 6,180,415). The Examiner alleged that Schultz et al. disclose a method for detecting the presence, and information about, a target having a molecular feature of interest, referring to col 5 and 6, col 34, line and 6-col 35 line 33 of Schultz et al. The Examiner also alleged that Schultz et al disclose

Joshua S. Salafsky and Kenneth B. Eisenthal  
Serial No.: 09/731,366  
Filed: December 6, 2000  
Page 11

contacting the target with one or more PRE's, Plasmon Resonant Particles, which the Examiner alleged are labels, having surface localized molecules to produce an interaction between the molecular feature and the localized molecules. The Examiner further alleged that Schultz et al disclose that the target contains a ligand-binding site, and the surface localized molecule is a ligand capable of forming a ligand/ligand-binding complex (col 5, lines 60-67). The Examiner alleged that Schultz et al disclose that the PRE's can accept pulses between 5 to 500 femtosecond for driving second harmonic generation processes, and contacting a surface with these PRE's thereby creating an interface at the surface which has target attached thereto wherein the target is not labeled with a non-linear label wherein the target is not detectable at the interface using a surface selective technique and wherein the target is labeled when the PRE comprising the ligand partner for the target attaches to the target and measuring a change in nonlinear optical light at the interface in the presence of the labeled target using a nonlinear optical technique. The Examiner also alleged that Schultz et al disclose that the PRE's can be used for cell sorting, and disclose analyzing a cell type expressing a particular surface antigen using a particular PRE probe, referring to col 49, lines 55-67.

With respect to second harmonic active-label as recited in the instant claims, the Examiner noted that in the specification on page 2, lines 19-23 the applicant defines that second harmonic active-labels are second harmonic moieties which can be attached to a molecule of interest that is not second harmonic active and applicant further defines, on page 8, lines 6-11, that a second harmonic refers to a frequency of light that is twice the frequency of a fundamental beam of light and that a second harmonic-active moiety is a substance which when irradiated with a fundamental beam of light

Joshua S. Salafsky and Kenneth B. Eisenthal  
Serial No.: 09/731,366  
Filed: December 6, 2000  
Page 12

generates a second harmonic of the fundamental. The Examiner then alleged that because Schultz et al disclose that the PRE's can accept pulses between 5 to 500 femtosecond for driving second harmonic generation, Schultz et al disclose second harmonic labels.

In response, applicants respectfully traverse the Examiner's position on the ground that Schultz et al. do not disclose a method comprising "using a surface selective technique," as recited in applicants' claims. Specifically, only noncentrosymmetric second harmonic generators can be used with a surface selective technique as recited in applicants' claims. See, for example, page 2, line 7-13 of the subject specification as well as **Exhibits A-D** submitted herewith. The PRE's of Schultz et al., however, can be "spherical" according to, for example, column 13, lines 9-1 of Schultz et al. As such, the PRE's of Schultz are useless in applicants' claimed method.

More importantly is that applicants are claiming a method which is neither taught nor suggested by Schultz et al. Nowhere do Schultz et al. teach or suggest using a surface selective technique, i.e. a technique requiring "hyperpolarizability and a net orientation at the interface," as pointed out on page 2, lines 9-10, and on page 2, line 33 to page 3, line 4 of applicants' specification.

Accordingly, Schultz et al. do not anticipate and do not make obvious applicants' claimed invention, and this rejection should be withdrawn.

#### Provisional Double Patenting

In Section 15 of the October 23, 2003 Office Action, the Examiner provisionally rejected claims 1-28 and 33-38 under the judicially created doctrine of obviousness-type double

Joshua S. Salafsky and Kenneth B. Eisenthal  
Serial No.: 09/731,366  
Filed: December 6, 2000  
Page 13

patenting as allegedly unpatentable over claims 1-17, 19, 24-49, 56-113, 131 and 132 of copending application No. 09/907,035. The Examiner alleged that although the conflicting claims are not identical, they are not patentable distinct from each other because both sets of claims are drawn to methods for detecting molecules at an interface using similar method steps. The Examiner noted that the instantly recited claims recite a second harmonic-active label while the 09/907,035 claims recite non-linear labels, and alleged that it is obvious to one skilled in the art that the non-linear labels encompass the second harmonic-active label.

In response, because all other rejections of the subject applications have been overcome as discussed above, applicants respectfully request that the Examiner issue the subject application pursuant to M.P.E.P. § 804(I)(E), which guides that:

The "provisional" double patenting rejection should continue to be made by the examiner in each application as long as there are conflicting claims in more than one application unless that "provisional" double patenting rejection is the only rejection remaining in one of the applications. If the "provisional" double patenting rejection in one application is the only rejection remaining in that application, the examiner should then withdraw that rejection and permit the application to issue as a patent, thereby converting the "provisional" double patenting rejection in the other application(s) into a double patenting rejection at the time the one application issues as a patent.

If the "provisional" double patenting rejections in both applications are the only rejections remaining in those applications, the examiner should then withdraw that rejection in one of the applications (e.g., the application with the earlier filing date) and permit the application to issue as a patent. The examiner should maintain the double patenting rejection in the other application as a "provisional" double patenting rejection which will be converted into a double patenting rejection when the one application issues as a patent. (Emphasis added).

Joshua S. Salafsky and Kenneth B. Eisenthal  
Serial No.: 09/731,366  
Filed: December 6, 2000  
Page 14

Furthermore, the allegedly conflicting claims in U.S. Serial No. 09/907,035 are also subject to being amended to the point of no longer being conflicting.

In conclusion, applicants respectfully submit that the amendment of the claims and the remarks herein overcome the rejections under 35 U.S.C. §§ 102, 103 and 112, leaving only the provisional double patenting rejection. However, pursuant to M.P.E.P. §804(I)(B), the provisional rejection should be withdrawn, allowing the subject application to proceed to issuance.

If a telephone interview would be of assistance in advancing prosecution of the subject application, applicants' undersigned attorney invites the Examiner to telephone him at the number provided below.

No fee is deemed necessary in connection with the filing of this Amendment. However, if an additional fee is required, authorization is hereby given to charge the amount of any such fee to Deposit Account No. 03-3125.

Respectfully submitted,

I hereby certify that this correspondence is being transmitted to the U.S. Patent and Trademark Office on the date indicated below by facsimile and is addressed to: Assistant Commissioner for Patents Washington, D.C. 20231 facsimile no. 703-672-9307.	
<i>Gary J. Gershik</i> 1/23/04	Date
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## **EXHIBIT A**



Table II. Parameters Used in the Extended Hückel Calculations

orbital	$H_H$ (eV)	$\zeta_1$	$\zeta_2$	$C_1^*$	$C_2^*$
Mo 4d	-12.30	4.54	1.90	0.5899	0.5899
5s	-9.66	1.956			
5p	-6.36	1.90			
W 5d	-10.40	4.98	2.07	0.6683	0.5422
6s	-8.62	2.34			
6p	-5.17	2.31			
P 3d	-7	1.4			
3s	-18.6	1.60			
3p	-14.0	1.60			
N 2s	-26.0	1.95			
2p	-13.4	1.95			
Cl 3s	-30.0	2.033			
3p	-15.0	2.033			
F 2s	-40.0	2.425			
2p	-18.1	2.425			

\*Coefficients used in the double- $\zeta$  expansion of the d orbitals.

In the case at hand of cyclic P containing compounds some interactions (15b) can be played out equally well by  $PX_2 \sigma^*$  as by 3d on P. But others (15a, 18) have no  $PX_2 \sigma^*$  symmetry equivalent. So P 3d orbitals could play a role, especially if the in-plane  $\pi$  system were important, as we concluded it is in  $(L_nMoN)_4$ . We repeated our calculations on  $(F_2PN)_4$  with 3d orbitals on P, placed at various energies. In each case a localized, bond-alternating structure is computed. But the degree of alternation is much smaller than in the transition-metal nitride case. We do not want to say that this is an argument against the involvement of 3d orbitals. More likely it is a failure of the extended Hückel method, or insufficient geometry optimization. The many known molecules may pucker to varying degrees, but they retain (with some exceptions) equal P-N bond lengths. We

would nevertheless keep an eye out for small bond alternation. To summarize: (1) There is an obvious analogy between d-p  $\pi$  orbitals of linear and cyclic early transition-metal nitrides and the p  $\pi$  orbitals of polyenes. This leads to predicted stability for some as yet unsynthesized MoN oligomers such as the cyclic trimer. (2) There should be a continuum of delocalization and tendency to localize or alternate bonds in cyclic heteromorphous systems. The 4n systems will localize by a second-order Jahn-Teller mechanism when the energy splitting between the (non-degenerate) nonbonding orbital combinations is relatively small. It is so in the  $(L_nMoN)_4$  system but not in  $(X_2PN)_4$ .

**Acknowledgment.** Funding for this work was provided by the Cornell University Materials Science Center through the National Science Foundation (Grant No. DMR821722A02). We thank Christine Gray for the typing and Jane Jorgensen and Elisabeth Fields for the drawings.

#### Appendix

The Extended Hückel method was used for all calculations.<sup>33</sup> Parameters<sup>34</sup> are listed in Table II. Mo-N and Mo-Cl bond lengths were taken from the  $[MoNCl_3O(C_4H_9)_2]_4$  X-ray structure.<sup>35</sup> Experimental bond lengths were also used for  $[W_3N_2Cl_4]^{2-}$ <sup>36</sup> and  $(F_2PN)_4$ .<sup>36</sup>

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*see next page*

## The Contribution of $\pi$ Electrons to Second Harmonic Generation in Organic Molecules

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Contribution from the Department of Applied Science, IBM Almaden Research Center, San Jose, California 95120, and the Institute of Physical Chemistry, University of Zurich, CH-8057 Zurich, Switzerland. Received June 28, 1985

**Abstract:** The frequency-dependent hyperpolarizability for sum frequency generation is calculated within a  $\pi$  electron approximation for a series of unsaturated organic compounds and compared to experimental data measured in polar and nonpolar liquid media. A procedure is also suggested to investigate the influence of electrostatic intermolecular interaction on the hyperpolarizability of small clusters of molecules in relative positions corresponding to the crystal structure.

### Introduction

For about a decade an active and systematic search has been conducted for materials exhibiting large optical nonlinear responses. Much attention has been given to organic compounds, view of their application to second harmonic generation (SHG) in the near infrared to the visible. It has been observed that ticular, noncentrosymmetric polar unsaturated molecules may exhibit unusually large hyperpolarizabilities.<sup>1-26</sup> Molecules in which intramolecular charge-transfer transitions occur and in which the dipole moments of the excited states are large appear to be particularly suited for this purpose. Efficient SHG furthermore requires the doubled frequency still to lie in the region

where the molecule is transparent; it should however not be too far removed from the lowest frequency transitions. There is every

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0007-2863/86/1102-5387\$01.50/0

indication that the lower excited states, which in the molecules of interest are mainly of  $\pi-\pi^*$  symmetry, make an important, if not the major, contribution to SHG in the wavelength range of interest.<sup>1,7,9,13,16,19-26</sup>

In the first part of this paper we calculate the contribution of the  $\pi$  electrons to the SHG tensor in a series of selected molecules by the PPP method. Our aim is to find an inexpensive computational procedure which gives correct orders of magnitude for the frequency-dependent hyperpolarizability and which reproduces correctly relative trends, such as substituent effects, within classes of similar compounds. This then should enable one to scan a variety of relatively large molecules and to provide a guidance in planning the synthesis of new chromophores with particular nonlinear optical properties. A number of computational investigations of SHG in organic compounds have been published by using the CNDO/S method<sup>14-16,24,25</sup> and the INDO method.<sup>20,21,25</sup> The explicit inclusion of the  $\sigma$  electrons makes these latter methods potentially more accurate than PPP, but the description of the  $\pi-\pi^*$  states is not necessarily always better, and the computational labor is significantly larger. The PPP method has already been used to assess the second-<sup>1</sup> and third-order<sup>1,27,28</sup> polarizability in various unsaturated hydrocarbons in a static electric field. To exhibit sum frequency generation in the liquid state, where there is random orientation, the molecules must be optically active. If both frequencies are the same, i.e., in the case of SHG, the effect altogether vanishes.<sup>29</sup> DC electric field induced second harmonic generation (EFISH) due to anisotropic averaging may be observed in the liquid state for molecules with a permanent dipole moment. This method has been widely applied to obtain an averaged value for the molecular hyperpolarizability.<sup>6,9,10,23,24,30-32</sup> The experimental values so obtained will serve as a comparison for our calculations on single molecules.

To be SHG active, crystals must belong to noncentrosymmetric space groups,<sup>29</sup> and evidently for all practical purposes the individual molecules in the crystal must also be noncentrosymmetric. However, it often occurs that noncentrosymmetric molecules crystallize in centrosymmetric space groups, making them useless, for our aims. In the preparation of new organic materials for SHG, the hyperpolarizability of the individual molecules is therefore not the sole criterion, but the relative spatial arrangement of the molecules within the crystal lattice is also of decisive importance. In an attempt to deduce the bulk hyperpolarizability, a first approximation consists in an additive superposition of the contributions of the individual molecules.<sup>33,34</sup> This approach

neglects the mutual influence of the molecules on each other, which undoubtedly may be important. A recent application of INDO and ab initio SCF methods to urea in the isolated and hydrogen-bonded crystalline state requires extensive computations.<sup>35</sup> In the second part of this paper we try to assess the importance of intermolecular interaction in the frame of the PPP model. By examining small clusters of molecules in the relative spatial positions dictated by the crystal structure and by including in the calculation electron repulsion terms also between atomic centers on different molecules, we study the changes induced in the tensor elements of the hyperpolarizability by electrostatic effects.

## II. Method of Calculation

The calculation of the sum frequency generation tensor

$$\chi_{ijk}^{(2)}(\omega_1 + \omega_2; -\omega_1, -\omega_2) = \beta_{ijk}$$

is based on the addition of six terms, as given by Ward<sup>36</sup> (Appendix 1). These expressions entail double summations over all eigenstates of the unperturbed molecular system considered. For practical reasons the infinite sums have to be truncated, and it has already been shown that a limited number of terms may lead to reasonable results.<sup>14,15</sup> If the frequencies of incident radiation  $\omega_1$  and  $\omega_2$  are set equal to zero, our adopted expressions do not automatically go into the correctly normalized formula for the static second-order hyperpolarizability. Strictly speaking, some normalization terms should be added,<sup>37</sup> which for simplicity are here neglected. Furthermore, the formula deduced in ref 36 are adequate as long as the radiation frequencies  $\omega_1$  and  $\omega_2$  are far removed from molecular resonances. Otherwise, if damping effects are to be included, one has to deal with eight terms<sup>38</sup> instead of the six terms mentioned above. Our routine computes the 27 tensor elements of  $\beta_{ijk}$  for eight pairs of frequencies  $\omega_1, \omega_2$ , which may be arbitrarily chosen but should not coincide with molecular resonances. This, nevertheless, allows one to investigate the dispersion of the hyperpolarizability tensor.

The basic quantities needed for the calculation of  $\beta_{ijk}$  are obtained through SCF-MO, single-CI calculations in the frame of the PPP approximation.<sup>39,40</sup> The molecular dipole moments are calculated within the ZDO approximation. On the other hand, the transition moments are computed in the dipole velocity form by an ab initio routine working in a Slater orbital basis.<sup>41</sup> Although this may seem inconsistent, it has been observed that in semicomplicated calculations of the kind used here, transition moments computed in the dipole vector form tend to be too large.

For our calculations we have essentially used standard parameters, and we have not calibrated them on measured hyperpolarizabilities, except for small adjustments described in Section III.

**Parametrization 1 (P1):** Valence state ionization potential,  $I_p$ , one-center electron repulsion integrals  $\gamma_{pq}$ , and resonance integrals  $\beta_{pq}$  are given in ref 42 and 43. The electron repulsion integrals  $\gamma_{pq}$  are computed by the charged sphere approximation.<sup>4</sup> These parameters have been quite successful in predicting electronic spectral properties and dipole moments of benzene derivatives with highly polar substituents<sup>42</sup> and of bile pigments.<sup>43</sup>

**Parametrization 2 (P2):** Valence state ionization potential, and one-center electron repulsion integrals are listed in ref 44, as deduced by Hinz and Jaffe. The resonance integrals are computed by the Wolfsberg-Helmholz formula<sup>45</sup> with a pro-

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# EXHIBIT B

# Effects on hyperpolarizabilities of molecular interactions in associating liquid mixtures

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(Received 29 March 1976)

We have measured the second and third order hyperpolarizabilities  $\beta$  and  $\gamma$  using the technique of electric field induced second harmonic generation in a variety of weakly associating (e.g., nitrobenzene-benzene) and strongly associating (e.g., water-methanol) liquid mixtures. These experiments are shown to yield interesting information on dipolar forces, hydrogen bonding, charge transfer interactions, and other solute-solute, solute-solvent effects.

## I. INTRODUCTION

The technique of electric field induced second harmonic generation in liquids<sup>1-4</sup> has proven to be extremely useful in the determination of both the second order  $\beta$  and third order  $\gamma$  hyperpolarizabilities. Extensive measurements<sup>5</sup> on both conjugated and nonconjugated organic molecules have elucidated the crucial role played by the delocalized  $\pi$ -electron contributions to these nonlinearities. As a result of these experiments, the close relationship between  $\beta$  and the donor-acceptor strength of a substituent on a benzene ring is now quantitatively understood.<sup>5,6</sup> In addition, measurements<sup>7</sup> using this technique on *ortho*, *meta*, and *para*-nitroaniline in the liquid state have led to a theoretical understanding of the importance of the intramolecular donor-acceptor charge transfer contribution to  $\beta$ . As a further extension of both experiment and theory, actual intermolecular charge transfer complexes (e.g., the classic pyridine-iodine system) have been investigated.<sup>8</sup>

As discussed previously,<sup>1,2</sup> nonlinear measurements of organic molecules in the liquid phase have many advantages over similar measurements in the gaseous or crystalline state. Namely, many of the most interesting highly conjugated molecules tend to readily decompose at the high temperatures required to vaporize them; however, they can be readily dissolved in an appropriate liquid solvent. Organic crystals, on the other hand, are difficult and time consuming to grow, and data analysis requires the knowledge of the crystal structure which may not have been determined. Another very important reason for studying molecular nonlinearities in the liquid phase is that chemical reactions occur most readily in this phase. Thus, measurements of electric field induced second harmonic generation in liquid mixtures or solutions can provide a means of obtaining information on molecular associations and correlations, intermolecular charge transfer interactions, hydrogen bonding, and dipolar interactions. Most previous work has concentrated on studying pure liquids and not mixtures. However, as we will show, mixtures can give important information on these molecular interactions.

## II. LOCAL FIELDS AND MOLECULAR CORRELATIONS

The polarization  $P_i$  produced in a molecule by an electric field  $E_j$  is given by

$$P_i = \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \gamma_{ijkl}E_jE_kE_l, \quad (1)$$

where the  $i, j, k, l$  refer to the molecular coordinate axes and,  $\alpha_{ij}$  is the usual linear polarizability of the molecule,  $\beta_{ijk}$  is the second order molecular hyperpolarizability, and  $\gamma_{ijkl}$  is the third order molecular hyperpolarizability. From the above equation we can see that  $\beta$  vanishes by symmetry in a molecule with a center of inversion (e.g., benzene) whereas  $\alpha$  and  $\gamma$  do not. Thus,  $\beta$  is particularly sensitive to interactions which remove such a center of symmetry.

The experimental technique of electric field induced second harmonic generation used to accurately determine these hyperpolarizabilities has been discussed in detail elsewhere,<sup>1</sup> and thus we only give a brief summary here. A static field  $E_0$  and a laser field  $E_\omega$  at frequency  $\omega$  (polarized along the direction of  $E_0$ ) applied to a liquid will produce a second harmonic polarization  $P_{2\omega}$  at frequency  $2\omega$  given by

$$P_{2\omega} = \Gamma E_0 E_\omega^2, \quad (2)$$

where  $\Gamma$  is the macroscopic third order nonlinearity of the liquid. For a pure liquid this macroscopic nonlinearity  $\Gamma$  is related to the microscopic hyperpolarizability  $\gamma$  of a single molecule via

$$\Gamma = N \gamma f_0^2 f_{2\omega}, \quad (3)$$

where  $N$  is the number of molecules/cm<sup>3</sup>, and the  $f$ 's are the local field factors evaluated at the frequency indicated. Equation (3) is only appropriate for nonassociating liquids. For a polar liquid there are two important contributions to  $\gamma$ , namely<sup>1,9</sup>

$$\gamma = \gamma_e + \mu \beta / 5kT, \quad (4)$$

where  $\gamma_e$  is the purely electronic average third order hyperpolarizability<sup>1,9</sup> (which does not vanish for centrosymmetric molecules) and where the temperature dependent rotational term is proportional to the dipole moment  $\mu$  and the vector part of the second order hyperpolarizability<sup>1,9</sup>  $\beta = (\beta_{xxx} + \beta_{xyy} + \beta_{yxx})$ , where  $x$  is along  $\mu$ . Since  $\beta$  does vanish in a centrosymmetric molecule (as  $\mu$  does) it is sensitive (for example) to chemical charge transfer interactions which remove this inversion center. For noninteracting mixtures Eq. (3) can be generalized to<sup>1</sup>

$$\Gamma_{mix} = \sum_i (N \gamma_i f_{0i}^2 f_{2\omega i}), \quad (5)$$

where the subscript  $i$  indicates that each factor in the

# EXHIBIT C

## THEORY OF SECOND-ORDER OPTICAL SUSCEPTIBILITIES OF BENZENE SUBSTITUTES

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Received 3 December 1974

We present a very simple model which describes the nonlinear susceptibilities of benzene substitutes as arising from the electromeric coupling of the  $\pi$ -electrons of the benzene ring with inductive radicals. Agreement between theory and experiment is excellent.

Recently a number of experimental studies of second harmonic generation (SHG) on both powder and single crystals have shown the anomalously high nonlinear optical response of some organic compounds [1-8]. High nonlinear coefficients have been found to be associated with strongly donor and acceptor substituents on aromatic molecules [4-5]. The recent experimental work of Hermann et al. [9] and the theoretical analysis of Rustagi and Ducuing [10] on third-order polarizabilities of organic conjugated molecules undoubtedly stress the fundamental role of electronic delocalization in high order susceptibilities. But molecular symmetry and requirements on orbital pairing [11] cause the  $\pi$ -electron contribution to second-order polarizabilities to vanish in majority of non-substituted conjugated molecules. Therefore the second-order optical effect of molecules with delocalized electrons may be thought to arise from the mesomeric effect [12]. In this letter we develop this basic idea and we present a very simple model which explains the quadratic susceptibilities of the benzene substitutes as arising from the coupling of the  $\pi$ -electrons system ( $\pi$ -ES) of the benzene ring with various radicals. First the model is presented, then we analyze from the point of view of the irreducible components of polarizability tensors [13] the most reliable experimental data on crystal susceptibilities. Finally theoretical and experimental results are compared and theoretical predictions are given.

In molecular crystals molecules are practically independent, as far as their electronic polarizabilities are

concerned. Therefore the second-order susceptibility tensor  $d$  can be written as the sum of the contributions  $\beta$  of individual molecules. This involves rotation of coordinate frames from molecular to crystal axes, which are most easily made by using irreducible tensor components [13-15] rather than cartesian components. In the transparency region the tensors  $d$  and  $\beta$  have ten independent components [16]. They can be written as the sum of two irreducible tensors [13], a vector (3 components) and a septor (7 components). These tensors belong to disconnected irreducible subspaces, so the vector (septor) part of  $d$  depends only on the vector (septor) part of  $\beta$ . In the present letter we only treat the vector part of nonlinearities, a more detailed analysis including the septor part will be given elsewhere [17].

Let us first consider the case of monosubstitutes. The centric benzene molecule may be decomposed into a skeleton [6 $\sigma$ (CC) and 6 $\sigma$ (CH) bonds] and a system of 6  $\pi$ -electrons. When a radical is substituted to one of the hydrogen atoms, the  $\sigma$  bonds are not strongly affected. Therefore one may assume that the  $\sigma$ -contribution to the quadratic polarizability of the substituted molecule is very small. Conversely, the  $\pi$ -ES is very sensitive to the substitution. It loses its center of symmetry and gains a proper dipole moment  $\Delta\mu$ , the so-called *electromeric dipole*, whose sign gives rise to the classification of substituent radicals into donor and acceptor groups [12]. In a benzene molecule the dipole induced on the  $\pi$ -ES by an electric field  $E$  is given by

$$p = \alpha E + \gamma E^2$$

where  $\alpha$  and  $\gamma$  are the polarizability and hyperpolarizability tensors, respectively. The axis joining the two radicals is labeled 3 and 3'. Then the

$$\alpha_{33} = \alpha_{11} + \alpha_{22}$$

$$\gamma_{333} = \gamma_{111} + \gamma_{222}$$

$$\gamma_{331} = \gamma_{112} + \gamma_{221}$$

We only consider that  $\alpha$  and  $\gamma$  are the

action of a very definite torsion of the axis due to a  $\Delta\mu \approx \alpha E_0$  response of the

$$p = \alpha E_T +$$

$$+ (\alpha + 3$$

In addition

$$\Delta\mu = \alpha E_0$$

the substituent linear polarizability response  $\beta$  is well-known of benzene harmonic result for a negligible  $\beta(2\omega) = \frac{1}{2}$  relation between  $\beta$  and the  $\alpha$   $6\gamma(3\omega)E$  of these  $\alpha$  the axis  $\pi$ -ES has The spectral direction

# EXHIBIT D

Published by The Chemical Society, Burlington House, London.  
Printed in England by The Triquet Press, Margate.

See next page

12123910525  
Price to non-fellows £4 10s. 0d. per annum  
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T-099 P. 024/025 F-865  
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## Molecular Hyperpolarisabilities

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### 1. Introduction

The idea that an atom or molecule may be distorted by a uniform electric field  $F$  (also a vector), and the proportionally constant  $\alpha$  (a second-rank tensor) is known as the *polarisability* of the system. Equation (1) is satisfactory for normal laboratory fields, but fails when the induced moment is comparable with a permanent molecular dipole. In strong fields, eqn. (1) becomes

$$m = \alpha F$$

(1)

where  $m$  (a vector) is the dipole moment induced in the system by the uniform electric field  $F$  (also a vector), and the proportionally constant  $\alpha$  (a second-rank tensor) is known as the *polarisability* of the system. Equation (1) is satisfactory for normal laboratory fields, but fails when the induced moment is comparable with a permanent molecular dipole. In strong fields, eqn. (1) becomes

$$m = \alpha F + \frac{1}{2} \beta F^2 + \frac{1}{6} \gamma F^3 + \dots$$

(2)

where the coefficients  $\beta$  and  $\gamma$  of the higher powers of  $F$  are referred to as the *first* and *second hyperpolarisabilities*, respectively. As shown in Section 2a,  $\beta$  is zero for systems with inversion symmetry, and the term involving  $\gamma$  then represents the initial deviation of  $m$  from a linear dependence on  $F$ . Figure 1 illustrates the dependence of  $m$  on  $F$ , obtained by substituting typical values of

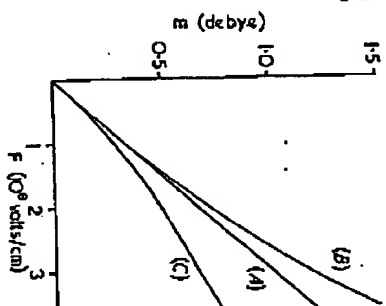


Fig. 1 Typical dependences of the induced moment  $m$  on electric field strength  $F$ . Values of  $\alpha$ ,  $\beta$ ,  $\gamma$  (in e.s.u.) are, respectively: curve (A)  $+10^{-18}$ , 0, 0; curve (B)  $+10^{-18}$ , 0,  $+10^{-28}$ ; curve (C)  $+10^{-18}$ ,  $-10^{-20}$ ,  $+10^{-28}$ .



$$\beta(CY_2X_2) = -(4/3)\beta_1 (4\beta_{C-X} - 4\beta_{C-Y}) \quad (13)$$

$$\beta_{12} - \beta_{21} (CY_2X_2) = (4/3)\beta_1 (4\beta_{C-X} + 4\beta_{C-Y}) \quad (14)$$

is application of the bond-additivity approximation to  $\gamma$ , defined in eqn. (6), in more straightforward, since  $\gamma$  is independent of the bond directions. For a substituted methane  $CY_nX_{4-n}$ , where  $n$  can take values from 0 to 4

$$\gamma(CY_nX_{4-n}) = n\gamma_C + (4-n)\gamma_X \quad (15)$$

parameters  $\gamma_C$  and  $\gamma_X$  can be evaluated from  $\gamma$  for  $CY_4$  and  $CX_4$ . Additivity rules could also be stated for the anisotropic components of  $\gamma$ , in which case the bond-additivity approximation are mentioned in subsections.

**Electrostatic Model.**—It is easy to understand qualitatively why a molecule have a second hyperpolarisability  $\gamma$ , since each of its component atoms on-averaging  $\gamma$ . In the case of  $\beta$ , however, the isolated atoms do not have a dipole moment, in order to investigate this, a simple electrostatic model of a molecule such as HCl is now considered.

large.  $\beta$  With centres separated by the internuclear distance  $R$  of the which they represent, as illustrated in Figure 3. It is assumed that the

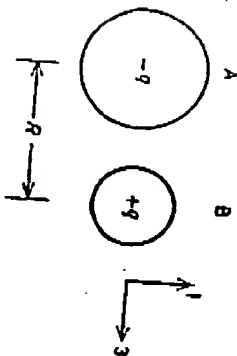


FIGURE 3. A simple model of a polar diatomic molecule.

and second hyperpolarisability  $\gamma^A$  of A are much greater than which are negligible. Such a model might represent HCl, but it is not a representation of  $CO_2$ , where the two atoms are of comparable size.  $\gamma$  of B produces an internal field  $F = -qR^{-2}$  along the z-axis, consideration of the two situations in which a uniform external field is applied parallel and perpendicular to the z-axis, the two components of  $\gamma$  are equal, for spatial degeneracy leads to energy terms in odd order of the field strength; see B. U. Cundon and G. H. Shortley, *Theory of Atomic Spectra*, University Press, 1935, ch. XV.

ponents of  $\beta$  emerge as  $\beta_{111} = \gamma^A F$  and  $\beta_{111} = \frac{1}{3}\gamma^A F$ . Hence the first hyperpolarisability of the model arises from the internal field  $F$  and the second hyperpolarisabilities of the component atoms. The anisotropy  $\Delta\beta$  of the model is zero and, when reasonable numerical parameters ( $q = \alpha \cdot 10^{-10}$  e.s.u.,  $R = \alpha \cdot 10^{-8}$  cm,  $\gamma^A = \alpha \cdot 10^{-30}$  e.s.u.) are inserted, the mean hyperpolarisability  $\beta$  of a molecule such as HCl should be  $\alpha \cdot 10^{-30}$  e.s.u. A negative sign for  $\beta_{111}$  implies that an external field acting along the dipole (from  $-$  to  $+$ ) induces a permanent moment. Similarly a negative  $\beta_{111}$  implies that a field perpendicular to the axis induces a dipole component antiparallel to the permanent moment.

**3 Determination of First Hyperpolarisabilities**  
Information concerning the first hyperpolarisability  $\beta$  of a number of simple molecules has been obtained by a variety of methods. Mean hyperpolarisabilities and other parameters are listed in Table 2. It should be stressed that some of the values are tentative. The methods by which the results have been obtained are discussed below.

**A. Quantum Mechanical Calculations.**—Third-order perturbation theory<sup>19</sup> for a molecule in a uniform static electric field gives, for the ground state,

$$\beta_{\alpha\beta\gamma} = \frac{S^2}{(W_1 - W_0)} \frac{\langle \psi_0 | \mu_\alpha | \psi_1 \rangle \langle \psi_1 | \mu_\beta | \psi_2 \rangle \langle \psi_2 | \mu_\gamma | \psi_0 \rangle}{(W_1 - W_0)^2} + \frac{S^2}{(W_2 - W_0)} \frac{\langle \psi_0 | \mu_\alpha | \psi_2 \rangle \langle \psi_2 | \mu_\beta | \psi_1 \rangle \langle \psi_1 | \mu_\gamma | \psi_0 \rangle}{(W_2 - W_0)^2} \quad (16)$$

where  $S$  denotes a sum of all permutations of the subsequent vector components, of the system, and  $W_i$  are the unperturbed energies of the ground and  $i$ th states ( $\psi_0$  and  $\psi_i$ ) elements  $\langle \psi_0 | \mu_\alpha | \psi_i \rangle$  have been written in the Dirac bracket notation. Approximate quantum mechanical calculations have been carried out<sup>20</sup> for methane, using eqn. (16), to yield  $\beta_{111} = -0.21 \times 10^{-30}$  e.s.u. Estimates of  $\beta$  and  $\Delta\beta$  for a number of polar diatomic molecules have recently been obtained from Hartree-Fock wave functions.<sup>20</sup>

**B. Second Harmonic Scattering.**—When a very intense beam of light, such as that produced by a pulsed ruby laser, passes through a fluid composed of molecules lacking inversion symmetry, a small fraction of the light is scattered at a frequency twice that of the incident radiation. The origin of the scattering may be understood in terms of a simple classical treatment (more rigorous theories have been given by Kielich,<sup>21</sup> Bersohn, Pao, and Frisch,<sup>22</sup> and others). If the incident radiation, propagating along the  $X$ -direction in space, is polarised with

<sup>19</sup> (a) I. M. O'Hare and R. P. Hargreaves, *J. Phys. Chem.*, 1967, 46, 2356.  
<sup>20</sup> S. Kielich, *Mol. and opt. Spectrosc.*, 1964, 13, 51.  
<sup>21</sup> (a) R. Bersohn, Y.-H. Pao, and H. L. Frisch, *J. Chem. Phys.*, 1966, 45, 3184.